NATURE INSPIRED HIERARCHICAL ARCHITECTURES FOR ADVANCED NANO-COMPOSITES

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The overall goal of this work is to investigate composite core structures having multi-scale hierarchical architecture, similar to those seen in many natural biological and geological systems. One obvious advantage is increase in interfacial area between the core and its surroundings (matrix phase or environment). This can drastically alter interface-related properties such as stress transfer, reactivity, thermal and electrical transport. This short paper demonstrates the dramatic change in mechanical behavior of a carbon-epoxy composite when the interface is altered by nanotube growth. Interfacial delamination is completely suppressed, and a normally brittle composite system becomes ductile. Future impact of these structures in biomedical, clean energy and environmental applications is discussed

Introduction:

A large variety of elegant and multifunctional composite structures seen in nature have hierarchical (capillary or dendrite-like) core structures that are intimately in contact with the matrix phase offering multi-scale reinforcement and energy exchange. If similar structures are adopted in synthetic composite systems, several advantages can be envisioned in terms of finer control of load transfer, thermal, electrical and mass transport, as well as extra interface for optimization of multiple properties. This concept sounds logical, but most materials fabrication techniques involve simpler and smoother surface geometries.

One option is to grow smaller nanotube-like structures on larger solids, preferably on porous solids offering higher-than-usual surface area to begin with, which can be subsequently infiltrated with the desired matrix or environmental fluid. However, very few studies report nanotube-attachment on solids (1-2), and none involve uneven porous substrates. Earlier studies also do not discuss the durability of CNT-substrate bond, which will be crucial for this approach. A possible reason for this may be that most bottom-up nanostructure growth techniques did not work well on porous solids. Recent developments in this group have made this possible, by using a reactive precursor on porous uneven structures that can subsequently allow growth of strongly attached nanotubes throughout the surface pores (3-4). This opens up a whole new design space for high surface area net shape core structures: start with a base porous material of required shape and size, attach nanotubes on them, and then infiltrate with necessary matrix.

Experiment:

The hierarchical structure discussed here is built by attaching carbon nanotubes (CNT) on microcellular graphite having open interconnected porosity. All data reported here was on one particular grade of graphitized foam (L1a provided by Koopers Inc. having density of about 0.4 g/cc, and porosity of about 80%). These foams are first coated with an oxide functional group in microwave plasma reactor, as described in earlier papers (4-5). The functionalized surface offers strong bonding and catalytic activity, so that a floating catalyst method (6-7) can be used to create strongly attached carbon nanotubes on them (3). Detailed micro-structural characterization has been performed using Field Emission Scanning Electron Microscopy (FE-SEM). Foams with and without attached nanotubes have been infiltrated with epoxy, cured, and the mechanical behavior of composites tested in compression. FE-SEM micrographs were used to perform comparative failure analysis of fractured surfaces.

Results and Discussions:

It must be noted that the goal of this study is to identify the influence of hierarchical attachments on the surface. Therefore all tests involved side-by-side comparison of as-received foams and nanotube-attached foams. Figure 1 shows the microstructure of the overall foam, along with higher magnification images of CNT attached to different regions. It can be seen that nanotubes are created even inside the deeper pores. Earlier studies have indicated (4) that these are pretty strongly attached to the graphite, and the underlying graphite layers get peeled off instead of individual CNTs.

Figure 2 shows the stress-strain plot for composite cubes made from these structures. Details of composite geometry have been discussed elsewhere (8). It is clear in these figures that the attachment of nanotubes convert the composite from normally brittle (Fig 2b) to ductile (Figure 2c).

Fracture surfaces of the composite are shown in Figure 3. They indicate that for composites made with untreated foam, epoxy is completely delaminated exposing the foam surface. On the other hand, composites made with CNT attached foam tend to hold on to the epoxy, and breakage occurs through the graphite.

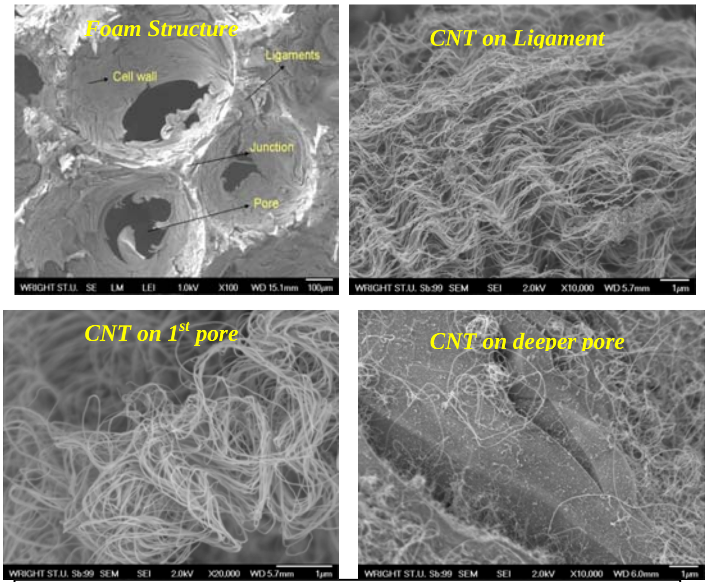

Fig 1: Micro-structure of the carbon foam, along with higher resolution images of nanotubes attached on different parts.

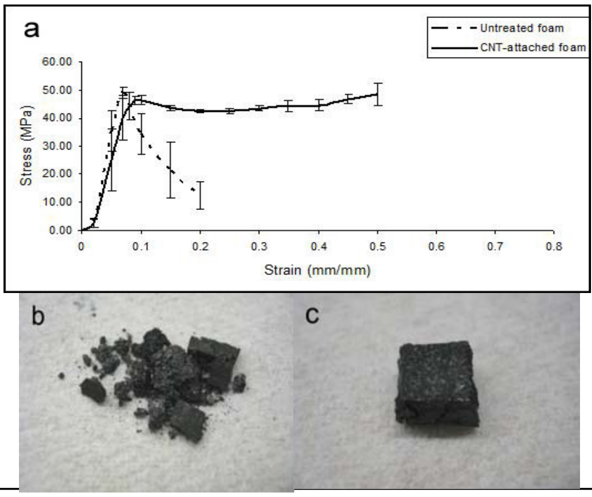

Figure 2: *Compression testing of foam-epoxy composite specimens having starting dimensions of 6 mm cube (a) stress-strain plots, (b) untreated foam-epoxy composite after testing (brittle composite is easily crushed), (b) composite made with CNT-attached foam after testing (significantly tougher composite that deforms without fracturing).*

These foam materials are now being tested as possible core or scaffolding for tissue and organic matter. Infiltration of bone cells through them is seen to be enhanced by the presence of CNT, indicating that they may be promising candidates for future biomedical composites. They have also been tested as support for metallic nano-catalyst particles such as Pd. CNT attachment is seen to significantly increase their electro-chemical and catalytic activities, making them suitable for porous electrodes in electrochemical devices, or as robust catalysts for water purification.

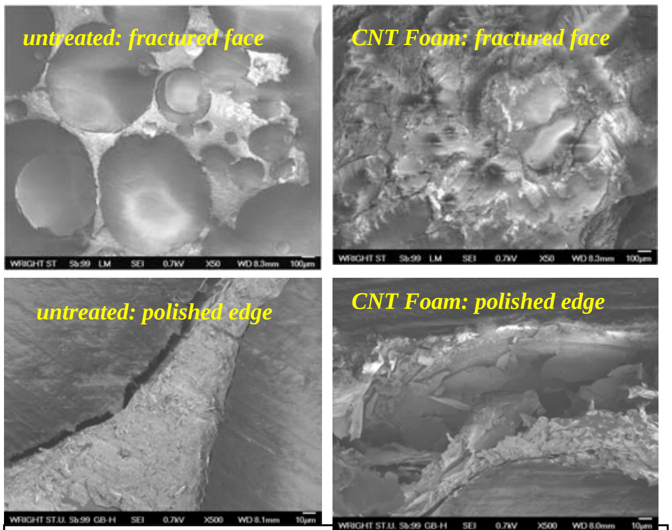

Fig 3- Microstructure of fractured surfaces: untreated foam (left) shows delamination between carbon and epoxy phases. CNT-attached foam (Right) shows no delamination and breakage through the graphitic phase.

Conclusions:

Synthetic composite structures having multi-scale hierarchical interfaces as in bio-composites are just beginning to evolve, and one option is to attach nanotubes on porous microcellular substrates. It is shown to convert a normally brittle carbon-epoxy composite system to a ductile one by preventing interfacial delamination. This opens up many future applications, some of whom are mentioned.

References:

1. *L. J. Ci, Z. G. Zhao, and J. B. Bai, Carbon 43 (2005) 855–894.*
2. *E. T. Thostenson, W. Z. Li, D. Z. Wang, and Z. F. Ren, J. Appl. Phys. 91 (9) (2002).*
3. *S. M. Mukhopadhyay, A. Karumuri and I. T. Barney, J. Phys. D: Appl. Phys. 42 (2009) 195503.*
4. *R. V. Pulikollu and S. M. Mukhopadhyay, Appl. Surf. Sci. 253 (2007) 7342-7352.*
5. *R. V. Pulikollu, S. R. Higgins and S. M. Mukhopadhyay, Surface & Coatings Technology 203 (2008) 65–72.*
6. *X. Li, A. Cao, Y. J. Jung, R. Vajtai, and P. M. Ajayan, Nano. Lett. 5 (2005) 1997-2000.*
7. *Cao, A.; Ajayan, P.M.; Ramanath, G.; Baskaran, R.; Turner, K., Appl. Phys. Lett., 2004, 84, 109.*
8. *S. M. Mukhopadhyay, A. Karumuri, J.Phys. D., in press.*

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